17th Group Elements :

Halogens
- F → [He] $2s^2 2p^5$
- Cl → [Ne] $3s^2 3p^5$
- Br → [Ar] $3d^{10} 4s^2 4p^5$
- I → [Kr] $4d^{10} 5s^2 5p^5$

At → [Xe] $4f^{14} 5d^{10} 6s^2 6p^5$

Called halogens since they are obtained from sea.

GEC = $ns^2 np^5$

- At is a radioactive metal

1. Occurrence

Relative abundance:

F ——Dec——→ I

Fluorine

- CaF_2 - fluorspar
- $3Ca_3(PO_4)_2 \cdot CaF_2$ - fluorapatite
- Na_3AlF_6 - cryolite

Chlorine

- NaCl - Rock salt
- KCl - Sylvine
- AgCl - Horn silver
- $KCl \cdot MgCl_2 \cdot 6H_2O$ → Carnallite

- Sea water contains 2.5 %. Bromine in the form of $NaBr$, KBr, $MgBr_2$
- Deep seaweeds contain 0.5 % Iodine in the form of iodides.
- Caliche (or) crude chile salt petre ($NaNO_3$) contains 0.2% Iodine in the form of $NaIO_3$
- Thyroxine in thyroid glands contain iodine.

General properties:

1. Vanderwaal's forces : $F_2 \xrightarrow{Inc} I_2$
2. M.P & BP : $F_2 \xrightarrow{Inc} I_2$

   (I_2 is a sublimable solid)
3. Physical state:

   F_2, Cl_2 (gas)

   Br_2 (liquid)

   I_2 (solid)
4. Metallic nature : $F_2 \xrightarrow{Inc} I_2$

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- All halogens are non-metals but I_2 exhibits some metallic properties like:

i) It is a violet lustrous solid

ii) It forms cations I^+ & I^{+3} ($ICl \rightarrow I^+ + Cl^-$)

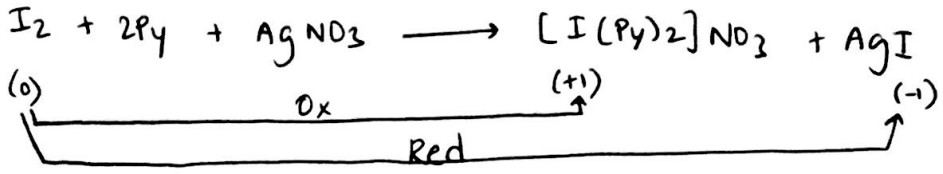
$ICN \rightarrow I^+ + CN^-$

$IPO_4 \rightarrow I^{+3} + PO_4^{3-}$

$I(CH_3COO)_3 \rightarrow I^{+3} + CH_3COO^-$

$I(IO_3)_3 \rightarrow I^+ + IO_3^-$

iii) Forms complexes



5. Covalent radius : $F_2 \xrightarrow{Inc} I_2$

- Atomic radius : $I_A \xrightarrow{Dec} VII_A \xrightarrow{Inc} O$

Since of $F_2 < Ne$
$Cl_2 < Ar$
$Br_2 < Kr$
$I < Xe$

In each period, halogen is the smallest element.

Reason: For halogens, covalent radius is taken while for noble gases Vanderwaal's radius is taken.

Vanderwaal's radius > Covalent radius

- Ionic radius : $F^- \xrightarrow{Inc} I^-$

- Size of $I^+ < I < I^-$

- IE of F > H > Cl > Br > I
- H^+ is formed :
  Reason: HE > LE
- X^+ doesn't form
  Reason: HE < LE
- I^+ is formed
  Reason: I^+ forms complexes

6. Ionization potential : $F \xrightarrow{Dec} I$

- In each period, halogen possesses higher IP next to noble gases.
- In VII A group, F has highest IP due to its small size
- Due to lower IP of I, it can form cations.

7. EN :

F	Cl	Br	I	At	
4.0	3.2	3	2.7	2.2	(Pauling's scale)

E.N (Mulliken) = 2.8 E.N (pauling)

8. Electron affinity :

$\boxed{Cl > F} > Br > I$ $\quad \Delta H_{(Eg)}$ dec

$\Delta H_{(-ve)}$ decreases

- EA of F < Cl

Reason: In F, the added e^- enters into compact 2p subshell. So there exist repulsions between the e^- already present and the added e^-. To overcome this, some of the energy released is used up. So net energy released is less than that of Chlorine

- Highest EA in LPT = Cl
- Halogens have higher EA values in each period because it is one e^- short of nearest inert gas configuration

9. Reactivity :

$F_2 \xrightarrow{\text{Dec}} I_2$

- F_2 is called super halogen due to its higher reactivity.

Reason: 1. Low B.E of F_2
2. F forms compounds with high coordination number & high LE

10. Nature of compounds :

- Metal - halogen compounds - Ionic (NaF, KCl, $MgCl_2$ etc)

Exception: $AlCl_3$ & $GaCl_3$ are covalent in anhydrous state but behave as ionic compounds in aqueous solutions due to higher hydration enthalpies of Al^{+3} & Ga^{+3}.

- Non-metal halogen compounds - Covalent (NCl_3, PCl_3, $AsCl_5$, SCl_2 etc)
- Halogen - Halogen → Non-polar covalent (Ex: F_2, Cl_2, Br_2 I_2)
  Polar covalent (Interhalogen compounds: ICl, ClF_3, IBr_3)
- Iodine compounds have some covalent nature
- CdI_2 has layer-structure.
- MP of $MF_2 > MI_2$

II. Oxidation states:

- F → 0 (F_2)
  -1 (compounds)
  OS of F in HOF = -1

- Cl → (+2 is not shown by any halogen)

0	-1	+1	~~+2~~	+3	+4	+5	+6	+7
Cl_2	HCl	HOCl		$HClO_2$	ClO_2	$HClO_3$	ClO_3	$HClO_4$

- Br →

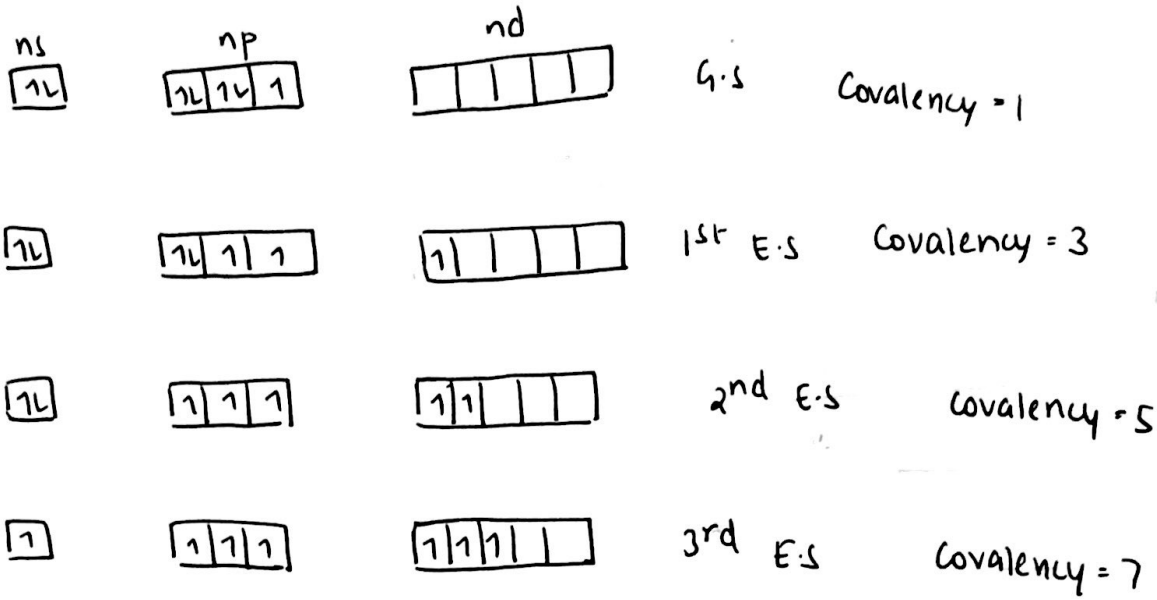
0	-1	+1	+3	+4	+5	+6	+7
Br_2	HBr	HOBr	$HBrO_2$	BrO_2	$HBrO_3$	BrO_3	$HBrO_4$ (very unstable)

- I →

0	-1	+1	+3	+5	+7
I_2	HI	HOI	HIO_2	HIO_3	HIO_4

- F exhibits unique O.S in its compounds.
- Halogens exhibit odd oxidation states.

- Max. covalency of F = 1
- F cannot extend its covalency due to the absence of d-orbitals.
- Cl, Br, I can extend their covalency due to the presence of d-orbitals.



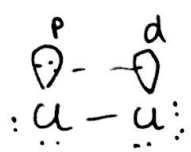
12. Bond-energy

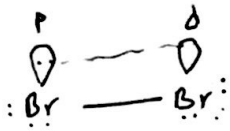
$$Cl_2 > Br_2 > \boxed{F_2} > I_2$$

- Bond energy of F_2 is less than that of Cl_2 & Br_2.

i) Mulliken's concept

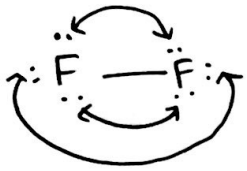
- Cl_2 & Br_2 have partial double bond character due to the possibility of $p\pi$-$d\pi$ back bonding.
- Such type of π-bonding is absent in F_2 due to the absence of d-orbitals.
- In I_2, even though there is possibility of $p\pi$-$d\pi$ overlapping, the bond energy is lower than F_2 due to large size of I atoms





ii) Coulson's concept:

According to Coulson, F is smaller in size. So the F-F bond distance is shorter and hence there exist greater repulsions among lone pairs of e^- present on two F atoms, which weakens the bond between 2 F atoms.



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13. Colours of halogens

F_2 - Pale yellow gas

Cl_2 - greenish yellow

Br_2 - reddish brown

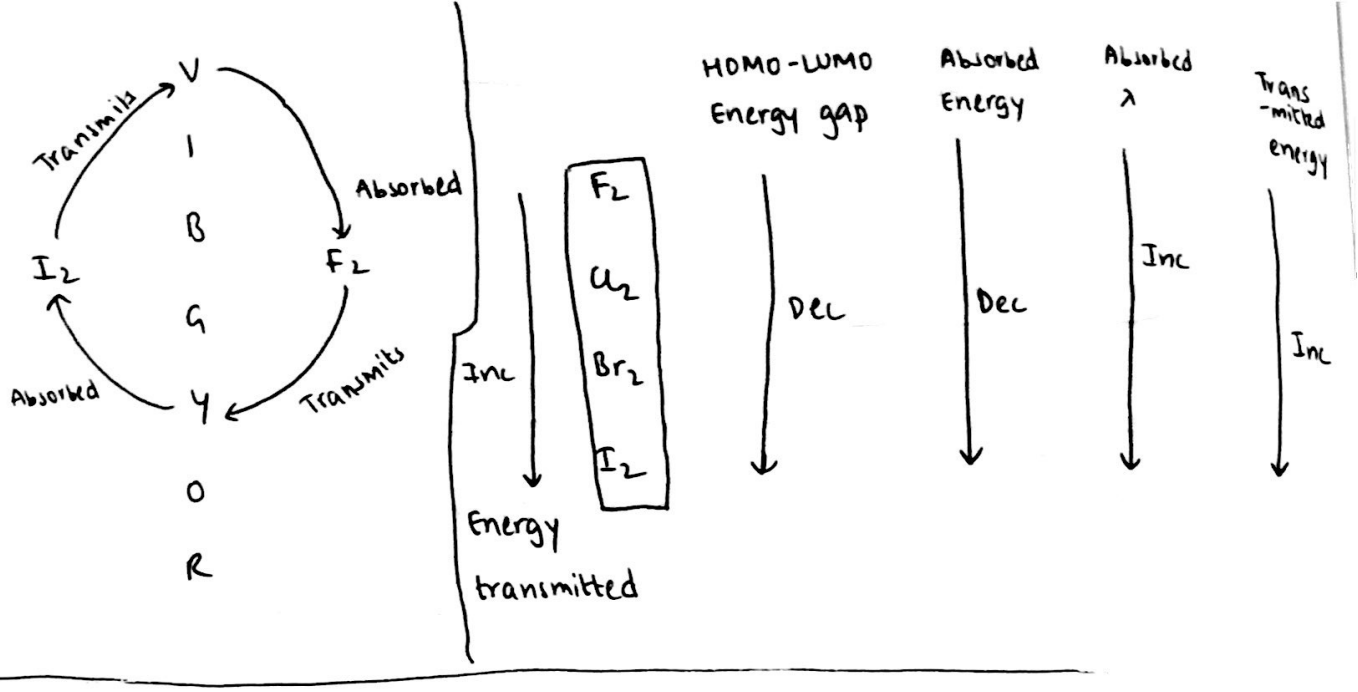
I_2 - violet

- F_2 (n=18) MOC = $\sigma_{1s}^2 \sigma_{1s}^{*2} \sigma_{2s}^2 \sigma_{2s}^{*2} \sigma_{2px}^2 \pi_{2py}^2 \pi_{2pz}^2 \pi^*_{2py}{}^2 \pi^*_{2pz}{}^2 \sigma^*_{2px}$

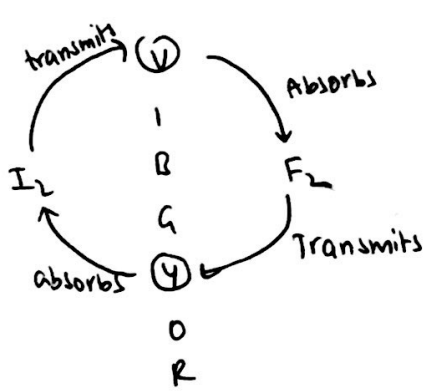
HOMO LUMO

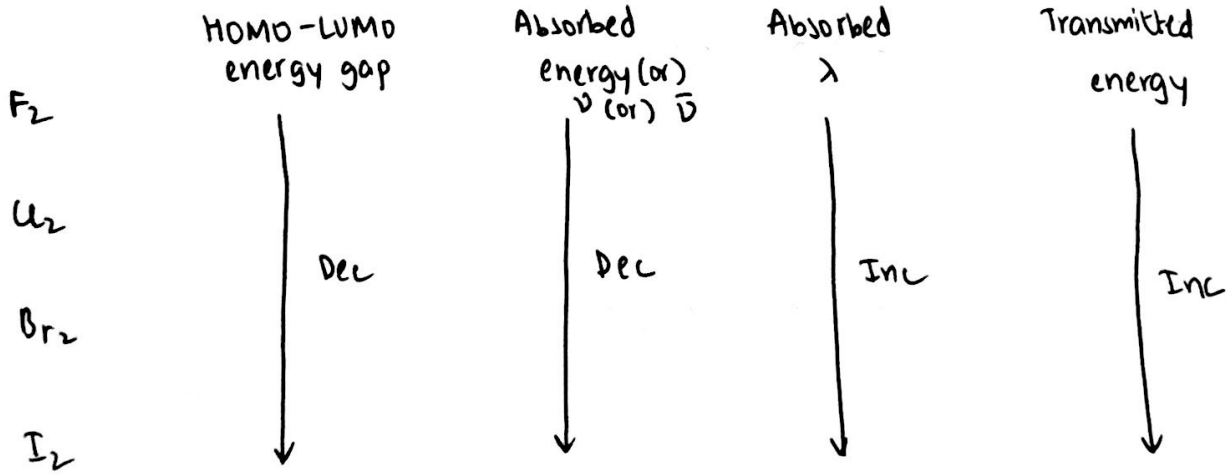
- HOMO - LUMO energy gap decreases from F_2 to I_2.

So F_2 absorbs higher frequency energy and transmits lesser energy



- Halogens absorb characteristic wavelengths from visible light so the e^- undergo transitions from HOMO to LUMO ($\pi^* \longrightarrow \sigma^*$) as a result of which they transmit their complementary colours.





Note: On moving from F_2 to I_2, the absorbed λ ~~decr~~ increases. This is called Bathochromic shift.

14. Oxidising power :

$$F_2 \xrightarrow{\text{Dec}} I_2$$

Reason: All halogens have +ve SRPs. The +ve SRP decreases from F_2 to I_2.

Oxidising power $\propto$ +SRP

- In ECs, F has highest SRP so it is a powerful oxidant.

- F has highest oxidising power.

Reason: F has highest +ve SRP amongst halogens, which is attributed to the following factors :

a) Most -ve $\Delta H^\circ_{X_2(g)} \longrightarrow X^-_{(g)}$

b) Most -ve ΔG° for conversion $X_{2(g)} \longrightarrow X^-_{(aq)}$

c) Lower bond dissociation enthalpy of F_2

d) Highest -ve hydration enthalpy of F^-

$$\tfrac{1}{2}X_{2(s)} \longrightarrow \tfrac{1}{2}X_{2(l)} \longrightarrow \tfrac{1}{2}X_{2(g)} \longrightarrow X_{(g)} \longrightarrow X^-_{(g)} \longrightarrow X^-_{(aq)} \quad ; \Delta H$$

$$\Delta H = \tfrac{1}{2}\Delta H_{fusion} + \tfrac{1}{2}\Delta H_{vap} + \tfrac{1}{2}\Delta H_{dissociation} + \Delta H_{EA} + \Delta H_{hyd}$$

$$= \frac{F}{2} + \frac{V}{2} + \frac{D}{2} - EA - HE$$

$$= -ve$$

$$\Delta G = \Delta H - T\Delta S \quad (\Delta S \text{ negligible})$$

$$\Delta G = \Delta H$$

$$-nFE = \Delta H$$

$$E = -\frac{\Delta H}{nF} \qquad \because \Delta H = -ve,\ E = +ve$$

- For F_2, Cl_2, $\Delta H = \frac{1}{2}\Delta H_{diss} + \Delta H_{eg} + \Delta H_{hyd}$ (since F_2, Cl_2 are gases)

For Br_2, $\Delta H = \frac{1}{2}\Delta H_{vap} + \frac{1}{2}\Delta H_{diss} + \Delta H_{EG} + \Delta H_{hyd}$ (since Br_2 is liq)

For I_2, $\Delta H = \frac{1}{2}\Delta H_{fusion} + \frac{1}{2}\Delta H_{vap} + \frac{1}{2}\Delta H_{diss} + \Delta H_{EG} + \Delta H_{hyd}$ (I_2 is solid)

15. Hydration energy

$$F^- \xrightarrow{\text{Dec}} I^-$$

16. Conductance / Conductivity:

- Solid I_2 conducts to some extent.

  Its conductance increases with increase in temp. and hence acts as intrinsic semiconductor.

- Liquid I_2 conducts slightly.

$$3I_2 \rightleftharpoons I_3^+ + I_3^-$$

17. Solubility:

- Br_2 & I_2 are more soluble in organic solvents like CCl_4

Hydrides (HX)

- Covalent hydrides

Prep:

HF

1. • $CaF_2 + H_2SO_4$ (conc) $\longrightarrow H_2F_2 + CaSO_4$ (H_2F_2 exists as dimer due to H-bond)

   • $2KHF_2 \xrightarrow{\Delta} 2KF + H_2F_2$

   • $H_2 + F_2 \longrightarrow 2HF$ (explosive even in the dark)

HCl

2. • $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$ (explosive)

   $H_2 + Cl_2 \xrightarrow{\text{dark}} 2HCl$ (slow)

   • $NaCl + H_2SO_4$ (conc) $\longrightarrow NaHSO_4 + HCl$

   • $2NH_4Cl + H_2SO_4$ (conc) $\longrightarrow (NH_4)_2SO_4 + 2HCl$

   NH_4HSO_4 is more soluble in H_2SO_4. So $(NH_4)_2SO_4$ is formed.

HBr

3. • $H_2 + Br_2 \xrightarrow{Pt} 2HBr$

   • $3NaBr + H_3PO_4$ (conc) $\longrightarrow Na_3PO_4 + 3HBr$ (H_3PO_4 is a weak OA)

   • $2P$ (red) $+ 3Br_2 \longrightarrow 2PBr_3 \xrightarrow{H_2O} H_3PO_3 + HBr$

4. **HI**

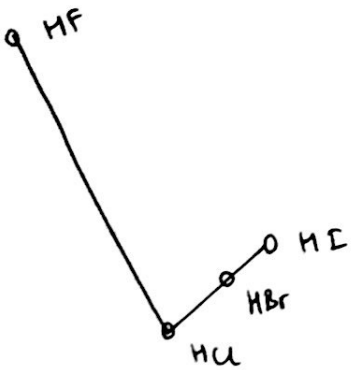
- $H_2 + I_2 \underset{450^\circ C}{\overset{Pt}{\rightleftharpoons}} 2HI$
- $3NaI + H_3PO_4 \text{ (conc)} \longrightarrow Na_3PO_4 + 3HI$
- $2P \text{ (red)} + 3I_2 \longrightarrow 2PI_3 \xrightarrow{H_2O} H_3PO_3 + HI$

Properties:

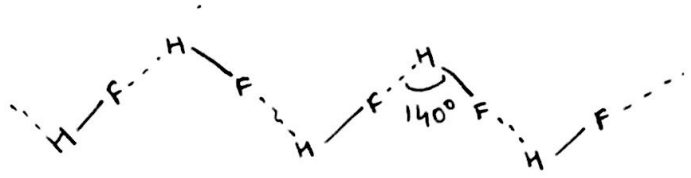
1. **Dipole moment** (Polarity): HF $\xrightarrow{Dec}$ HI
2. **Covalent nature**: HF $\xrightarrow{Inc}$ HI

   Ionic nature: HF $\xrightarrow{Dec}$ HI
3. **Thermal stability**: HF $\xrightarrow{Dec}$ HI

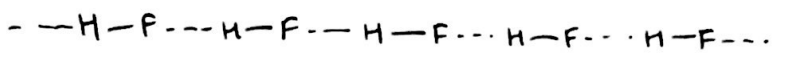
   Reason: Bond energy decreases.
4. **Reducing nature**: HF $\xrightarrow{Inc}$ HI
5. **B.P**



- Abnormally higher BP of HF is due to H-bonding.
- HF has H-bonds in solid, liquid & gas phases.



(solid)



(liquid & gas)

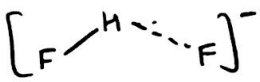
- In gas phase, $(HF)_6$, $(HF)_2$, HF exist.
- HF forms stronger H-bonds

  Reason: H-F bond is highly polar
- H-bond strength:

  H---F—H > H---O—H > H---N—H
- B.P of H_2O > HF (1. since H_2O has more no. of H-bonds)
  2. H_2O exists as discrete molecules in vapour phase while HF exists as polymer

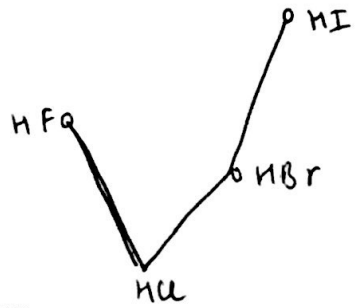
HF

- Hydrofluoric exists as a dibasic acid H_2F_2 due to H-bonds.
- H_2F_2 (HF) can form $HF_2^{\ominus}$ (or) KHF_2 due to H-bonding.



- HBr_2^-, HCl_2^-, HI_2^- are not known due to the absence of H-bonding.

6. MP



- Abnormally higher MP of HF is due to H-bond

7. **Volatility:**

$$\text{Volatility} \propto \frac{1}{BP}$$

Volatility of : $HF < HI < HBr < HCl$

8. **Physical state:**

$HF \rightarrow$ liq

$HCl, HBr, HI \rightarrow$ gases

} → at room temp.

9. **Acidic nature:**

$$HF \xrightarrow{\text{Inc}} HI$$

Reason: Bond energy decreases

- ~~HF_2~~ Hydrofluoric acid exists as a dibasic acid H_2F_2. So, it forms two series of salts.

  KHF_2 (Acidic salt)

  KF (normal salt)

- $HX \cdot nH_2O \xrightarrow[-nH_2O]{} HX_{(g)} \longrightarrow H_{(g)} + X_{(g)}$

  $H_{(g)} \rightarrow H^+_{(g)} \rightarrow H^+_{(Aq)}$

  $X_{(g)} \rightarrow X^-_{(g)} \rightarrow X^-_{(Aq)}$

$$\Delta H_{total} = \Delta H_{dehydration} + \Delta H_{dissociation} + \Delta H_{ionization(H)} + \Delta H_{EA(x)} + \Delta H_{hyd(H^+)} + \Delta H_{hyd(x^-)}$$

$$= (+DH) + (D) + (+I) + (-EA) + (-HE_{(H^+)}) + (-HE_{x^-})$$

ΔH_{total} = -ve

- $\Delta H_{dehydration}$: HF >> HI > HBr > HCl
- ΔH_{total} (-ve value) : HF $\xrightarrow{Inc}$ HI
- $T\Delta S$ = +ve value : HF $\xrightarrow{Inc}$ HI
- ΔG_{total} (-ve value) : HF $\xrightarrow{Inc}$ HI

- As ΔG° -ve value increases from HF to HI, the acidic strength increases.

HF

- HF slightly ionizes in water. So it is a very weak acid.

$$HF \rightleftharpoons H^+ + F^-$$

- HCl, HBr & HI completely ionize in water.

$$HX \longrightarrow H^+ + X^- \quad (X = Cl, Br, I)$$

Acidic strength in H_2O : HCl = HBr = ~~HI~~ HI = $[H_3O^+]$

Acidic strength in glacial acetic acid: HF << HCl < HBr < HI
(poor H+ acceptor)

- Mineral acids HCl, HNO_3 & H_2SO_4 dissolve in HF (except $HClO_4$)
  ↓ higher acidic strength

Reason: HF forces mineral acids to accept a proton.

∴ HF is an Bronsted acid while HCl, HNO_3, H_2SO_4 behave as Bronsted bases.

HF → strong Bronsted Acid

HCl, HNO_3, H_2SO_4 → Bronsted bases

- In the presence of fluoride acceptors BF_3, NbF_5, SbF_5, AsF_5, HF acts as Lewis base.

$$\underset{(LB)}{HF} + \underset{(LA)}{BF_3} \longrightarrow H^+ + BF_4^-$$

- HF acts as a non-aqueous solvent due to self ionization.

$$HF + HF \rightleftharpoons H_2F^+ + F^-$$

- HF is a bad conductor of electricity.

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- No oxidant can oxidise HF to F_2

  Reason: F_2 is the most powerful oxidant.

- HF attacks glass (SiO_2)

$$4HF + SiO_2 \longrightarrow SiF_4 + H_2O$$

$$SiF_4 + 2HF \longrightarrow H_2SiF_6 \quad \text{(soluble complex)}$$

∴ HF is used for etching of glass

- $HF + CCl_4 \xrightarrow[SbF_5]{\text{Anh. condition}} \underset{\text{(Freon)}}{CCl_2F_2} + HCl$

- HF is used for etching, pickling of steel & manufacture of herbicides

HCl

- Strong oxidants MnO_2, PbO_2, Pb_3O_4, $KMnO_4$, $K_2Cr_2O_7$ oxidise HCl to Cl_2

HBr

- HBr is a stronger reducing agent than HCl

$$HBr + \underset{(\text{conc})}{H_2SO_4} \longrightarrow Br_2 + SO_2 + H_2O$$

$$2HBr + \underset{(\text{Air})}{O_2} \longrightarrow Br_2 + H_2O$$

HI

- HI is a very powerful reducing agent.

$$H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + H_2O$$

- $SO_2 \xrightarrow{HI} S \xrightarrow{HI} H_2S$

- $HNO_3 + HI \longrightarrow NO_2 + \frac{1}{2}I_2 + H_2O$

$$HNO_2 + HI \longrightarrow NO + \tfrac{1}{2}I_2 + H_2O$$

- HI reduces Fe^{+3} to Fe^{+2}

$$FeCl_3 + 2HI \longrightarrow FeCl_2 + I_2 + 2HCl$$

- HI reduces $K_2S_2O_8$ to K_2SO_4

~~$HI + K_2S_2O_8 \longrightarrow K_2SO_4 +$~~

$$2I^- + S_2O_8^{2-} \longrightarrow 2SO_4^{2-} + I_2$$

- F_2 displaces other halogens from HX

$$F_2 + 2HX \longrightarrow 2HF + X_2 \qquad (X = Cl, Br, I)$$

- ΔH_f° = -ve HF $\xrightarrow{\text{Dec}}$ HI (Thermal stability decreases)

- conc. HCl liquid has yellow colouration due to Fe^{+3}
- HF is stored in a vessel made of Cu or Monel metal (Cu + Ni + Fe)
- Azeotropic compositions :

	HF	HCl	HBr	HI
	35·8%	20·4%	47%	57%
Azeotropic BP :	120°C	110°C	126°C	127°C

FLUORINE (F_2)

- Pale yellow gas
- BP = −188°C
- FP = −239°C
- Poisonous
- HF is more poisonous than F_2

- Difficulties involved in isolation of F_2 :

1. F_2 attacks almost all materials.

$$\text{Graphite (C)} + 2F_2 \longrightarrow CF_4$$

$$Pt + F_2 \longrightarrow PtF_4$$

$$SiO_2 + F_2 \longrightarrow SiF_4$$

2. HF is hard to oxidise into F_2.

   Reason: No oxidant can oxidise HF

3. Anhydrous fused HF is a bad conductor of electricity. So manufacture of F_2 by the electrolysis of fused HF is not possible.

4. Aq. HF is a very good conductor of electricity. The F_2 produced during electrolysis reacts with water.

$$F_2 + H_2O \longrightarrow \underbrace{O_2 + O_3}_{\downarrow}$$

ozonized oxygen.

- Moissan for the first time isolated F_2.

- **Moissan's method**

Electrolyte : $(KF + HF) \rightarrow$ Fused
1 : 13

Electrodes : Pt-Ir

Electrolytic cell : Pt-Ir

Temp : $-23^\circ C$ in CH_3Cl bath

$$H_2F_2 \longrightarrow 2H^+ + 2F^-$$

Anode : $2F^- \longrightarrow F_2 + 2e^-$

Cathode : $2H^+ + 2e^- \longrightarrow H_2$

Common to all manufacture methods

- F_2 is made free from HF by passing through NaF

$$NaF + HF \longrightarrow NaHF_2$$

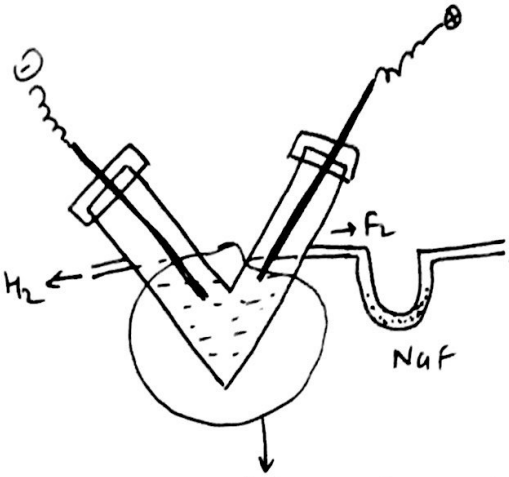
- In this method, 5 g Pt is lost per 1 g preparation of F_2.

- **Dennis method**

Electrolyte : Fused KHF_2

Anode & Cathode : Graphite rods

Electrolytic cell : V-shaped copper tube covered with asbestos



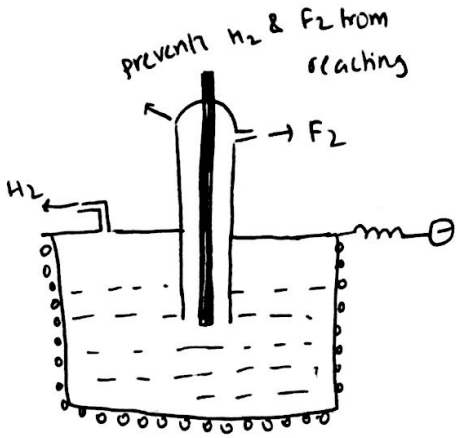
3. Whytlaw Grey's method

Electrolyte : Fused KHF_2

Anode : Graphite rods

Cathode : Copper electrolytic cell

Anode & Cathode are separated by a copper diaphragm.



$NaF + HF \longrightarrow NaHF_2$

4. Modern method

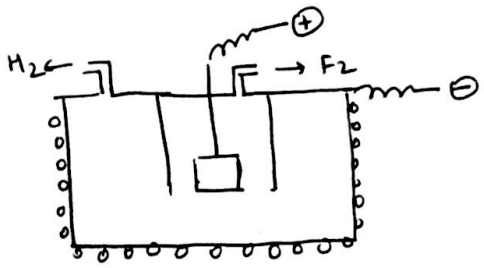
Electrolyte: Fused (KF + HF) in 1:2 Temp: 70-80°C

Anode: Petroleum coke (c) impregnated with copper

Cathode: Steel cell

- Valves are made up of Cu (or) Monel metal (Cu + Ni + Fe) since a protective layer is formed

- Teflon coated gaskets are used.
- A steel cylinder fitted to the lid separates anode & cathode.



Prep. methods

- $K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_4$

$$MnF_4 \downarrow$$

$$MnF_3 + \tfrac{1}{2} F_2$$

Chemical properties:

1. With H_2O:

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

$$3F_2 + 3H_2O \longrightarrow 6HF + O_3$$

$$5F_2 + 5H_2O \longrightarrow 10HF + (O_3 + O_2)$$

($O_3 + O_2$): ozonized oxygen

*

2. With NH_3:

a) $3F_2 + NH_3 \longrightarrow NF_3 + 3HF$

($3F_2$: excess)

b) $3F_2 + 2NH_3 \longrightarrow N_2 + 6HF$

($2NH_3$: excess)

***

3. With NaOH / KOH

a) $2NaOH$ (cold dil) $+ 2F_2 \longrightarrow 2NaF + \boxed{OF_2}\uparrow + H_2O$

b) $NaOH$ (hot conc) $+ F_2 \longrightarrow NaF + O_2 + H_2O$

4. With metals:

- $2Na + F_2 \longrightarrow 2NaF$
- $2Al + 3F_2 \longrightarrow 2AlF_3$
- $Cu + F_2 \longrightarrow CuF_2$ (Cu_2F_2 doesn't exist as F_2^- oxidises Cu)

** $\boxed{Cu, Ni, Fe, Al}$ form a protective fluoride film on their surfaces which prevents further attack. So F_2 can be stored in vessels made up of these metals.

5. With Non-metals:

- $2B + 3F_2 \longrightarrow 2BF_3$
- $S + F_2 \longrightarrow SF_6$
- $N_2 + 3F_2 \longrightarrow 2NF_3$

- N_2 & O_2 don't react with F_2 at room temp. (Higher bond energy)
- F_2 doesn't react with He, Ne, Ar

$$F_2 + Kr \longrightarrow KrF_2$$

$$F_2 + Xe \longrightarrow XeF_2$$

$$2F_2 + Xe \longrightarrow XeF_4$$

$$3F_2 + Xe \longrightarrow XeF_6$$

Displacement reactions (Oxidation)

- $F_2 + 2KCl \longrightarrow 2KF + Cl_2$
- $F_2 + 2KBr \longrightarrow 2KF + Br_2$
- $F_2 + 2KI \longrightarrow 2KF + I_2$

Oxidizing properties

- $KClO_3 + H_2O + F_2 \longrightarrow KClO_4 + 2HF$

  $KIO_3 + H_2O + F_2 \longrightarrow KIO_4 + 2HF$

($KBrO_4$ is not known. Br doesn't show +7 O.S)

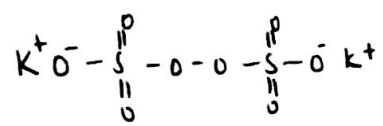
- $H_2S + 4F_2 \longrightarrow SF_6 + 2HF$
- $Cr^{+3} + H_2O + F_2 \longrightarrow Cr_2O_7^{2-} + H^+ + F^-$
- $CH_4 + 2F_2 \longrightarrow C + 4HF$

  $C + 2F_2 \longrightarrow CF_4$

***

- $2KHSO_4 + F_2 \longrightarrow K_2S_2O_8 + 2HF$

Potassium per disulphate



Uses:

- NaF, Na_3AlF_6 - insecticides
- CuF_2 - ceramic industry
- $(C_2F_4)_n$ - PTFE (poly tetra fluoro ethylene) - Teflon (anti corrosion $\{CF_2-CF_2\}$)
- Freons - CCl_2F_2 - refrigerant
- SF_6 - gaseous insulator
- DDFT - poison like DDT
- UF_6 - separation of isotopes of Uranium

**
- HF - glass etching

F_2 free from HF cannot attack glass

Below 100°C, F_2 reacts slowly with glass. Above 100°C, reaction is fast.

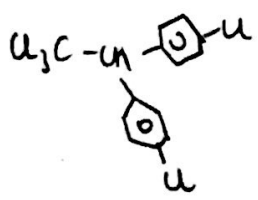
*****
- For making fluorinating agents.

$$CH_3OH + 8F_2 \xrightarrow[(Ag \text{ in } +2 \text{ state})]{AgF_2} CF_3OF + 4HF$$

CF_3OF ↓ powerful OA

- MgF_2 - optical industry
- SbF_3 - pottery & porcelein industry
- $CH_3COONa \cdot NaF \rightarrow$ rat poison

- DDT - Dichloro diphenyl trichloroethane



CHLORINE (Cl_2)

- greenish yellow gas
- BP = $-34.6^{\circ}C$
  MP = $-101.1^{\circ}C$
- 2.4 times heavier than air
- When passed through cold water, forms $\boxed{Cl_2 \cdot 8H_2O}$ hydrate
- Cl_2 is toxic to lungs, throat and mucus membrane.

Prep:

1. $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$ (Weldon's)

2. $4HCl + O_2 \xrightarrow[\Delta]{CuCl_2} Cl_2 + 2H_2O$ (Deacon's)

$$CuCl_2 \xrightarrow{\Delta} Cu_2Cl_2 + Cl_2$$

$$Cu_2Cl_2 + O_2 \longrightarrow CuO \cdot CuCl_2$$

$$CuO\,CuCl_2 + 2HCl \longrightarrow Cl_2 + 2Cu_2Cl_2 + H_2O$$

3. $K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 3Cl_2 + 7H_2O$

(Cl: -1 on the left, 0 on the right)

$n_f = 1e^- \times \frac{6}{14}$

$$E_{HCl} = \frac{M}{3/7}$$

$$KMnO_4 + HCl \longrightarrow KCl + MnCl_2 + Cl_2 + H_2O$$

4. $PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2 + 2H_2O$

$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + Cl_2 + 4H_2O$

5. $O_3 + 2HCl \longrightarrow Cl_2 + H_2O + O_2$

6. $NaOCl + 2HCl \longrightarrow NaCl + Cl_2 + H_2O$

* 7. $CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + Cl_2 + H_2O$
(excess of dil. acid)

$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + Cl_2$

8. $MnCl_2 + Ca(OH)_2 \longrightarrow Mn(OH)_2 + CaCl_2$

$Mn(OH)_2 + \frac{1}{2}O_2 \longrightarrow MnO_2 + H_2O$
(Air)

$MnO_2 + Ca(OH)_2 \longrightarrow CaMnO_3 + H_2O$
(Calcium manganite)

$CaMnO_3 + HCl \longrightarrow CaCl_2 + Cl_2 + MnCl_2 + H_2O$
(dil)

* 9. $PtCl_4 \xrightarrow{\Delta} Pt + 2Cl_2$
(Pure)

$AuCl_3 \xrightarrow{\Delta} Au + \frac{3}{2}Cl_2$
(Pure)

*** H_2O_2, SO_2, H_2S reduce $Cl_2 \longrightarrow HCl$ & $Br_2 \longrightarrow HCl$

They can't oxidise HCl to Cl_2

H_2O_2, SO_2, H_2S : $Cl_2 \longrightarrow HCl$

$Br_2 \longrightarrow HBr$

10. $NaCl + H_2SO_4 + MnO_2 \longrightarrow Cl_2 + NaHSO_4 + MnSO_4 + H_2O$

Manufacture :

1. Nelson's cell

Electrolyte : Brine soln. (Aq. NaCl)

Anode : Graphite

Cathode : Perforated steel U-tube

$2NaCl \longrightarrow 2Na^+ + 2Cl^-$ $\qquad$ $H_2O \longrightarrow H_3O^+ + OH^-$

Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode : $H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

$2Na^+ + 2OH^- \longrightarrow 2NaOH$

$n_{Cl_2} : n_{H_2} : n_{NaOH} = 1 : 1 : 2$

Side reaction:

$Cl_2 + NaOH \longrightarrow NaCl + NaOCl + H_2O$

2. Castner - Kellner's process (Mercury cathode process)

- In outer compartments, the same reactions as above.

Electrolyte : Brine soln.

Anode : Graphite : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode : Hg : $2Na^+ + 2e^- \longrightarrow 2Na$ (over-voltage phenomenon Na gets discharge)

$2Na + Hg \longrightarrow Na_2Hg$

3. Down's process

Electrolyte : Fused NaCl $\quad 2NaCl \longrightarrow 2Na^+ + 2Cl^-$

Anode : Graphite : $2Cl^- \longrightarrow Cl_2 + 2e^-$

Cathode : Iron : $2Na^+ + 2e^- \longrightarrow 2Na$

***

4. Nitrosyl chloride method

$$3HNO_3 + 3NaCl \longrightarrow 3NaNO_3 + NOCl + Cl_2 + 2H_2O$$

$$2NOCl + O_2 \longrightarrow 2NO_2 + Cl_2$$

Chem. properties:

**

1. With water :

$$Cl_2 + H_2O \longrightarrow \underbrace{HCl + HOCl}_{\text{chlorine water}}$$

$$HOCl \longrightarrow HCl + (O)$$

(unstable)

The nascent oxygen is responsible for disinfectant action of Cl_2 water.

*

2. With ammonia

a) $NH_3 + 3Cl_2 \longrightarrow NCl_3 + 3HCl$

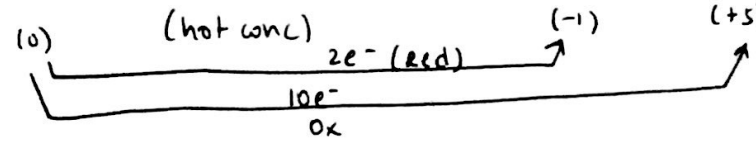
(excess) (explosive)

b) $8NH_3 + 3Cl_2 \longrightarrow N_2 + 6NH_4Cl$
(excess)

*
3. With alkalis

a) $Cl_2 + 2NaOH \longrightarrow NaCl + NaOCl + H_2O$ (DPP)
(dil & cold)

b) $3Cl_2 + 6NaOH \longrightarrow 5NaCl + NaClO_3 + 3H_2O$
(hot conc)



$E_{Cl_2\ (oxidant)} = \frac{M}{2}$
gets reduced

$E_{Cl_2\ (Reductant)} = \frac{M}{10}$

$E_{Cl_2\ (DPP)} = \frac{M}{2} + \frac{M}{10} = \frac{3M}{5}$

- In hot soln, hypochlorite disproportionates to Cl^- and ClO_3^-

c) $Ca(OH)_2 + Cl_2 \longrightarrow CaCl_2 + Ca(OCl)_2 + H_2O$
(cold dil)

d) $Ca(OH)_2 + Cl_2 \longrightarrow CaCl_2 + Ca(ClO_3)_2 + H_2O$
(hot conc)

***
e) $Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 \cdot H_2O$
(dry slaked lime) (dry) (Bleaching powder)

4. With metals:

- $Ca + Cl_2 \longrightarrow CaCl_2$
- $2Al + 3Cl_2 \longrightarrow 2AlCl_3$
- $Fe + Cl_2 \longrightarrow FeCl_3$ (Cl_2 is OA so $FeCl_2$ only forms)
  ↓ X
  $FeCl_2$
  In higher OS
- $Cu + Cl_2 \longrightarrow Cu_2Cl_2$ ✗ (Higher OS)
  $\longrightarrow CuCl_2$ ✓

*
- $Fe + 2HCl \longrightarrow FeCl_2 + H_2$ ($FeCl_3$ doesn't form as liberated H_2 is reducing)

5. With non-metals:

- $2P + 3Cl_2 \longrightarrow 2PCl_3$
- $2S + Cl_2 \longrightarrow S_2Cl_2$
- $S_2Cl_2 + Cl_2 \longrightarrow 2SCl_2$
- $2B + 3Cl_2 \longrightarrow 2BCl_3$

Addition rxns:

- $CO + Cl_2 \xrightarrow{h\nu} COCl_2$
- $SO_2 + Cl_2 \xrightarrow{\text{charcoal}} SO_2Cl_2$
- $2NO + Cl_2 \xrightarrow{h\nu} 2NOCl$

- Cl_2 doesn't combine directly with N_2, O_2, C.
- Doesn't react with noble gases.

6. Displacement reactions (Oxidation)

- $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$
- $2KI + Cl_2 \longrightarrow 2KCl + I_2$

7. Oxidising properties:

- $H_2S + Cl_2 \longrightarrow 2HCl + S$ (With F_2, SF_6 forms)
- $2FeCl_2 + Cl_2 \longrightarrow 2FeCl_3$

  $2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$
- $NaNO_2 + H_2O + Cl_2 \longrightarrow NaNO_3 + 2HCl$

  $Na_3AsO_3 + H_2O + Cl_2 \longrightarrow Na_2AsO_4 + 2HCl$

  $Na_2SO_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + 2HCl$

*
- $Na_2S_2O_3 + H_2O + Cl_2 \longrightarrow Na_2SO_4 + S + 2HCl$
- $SO_2 + Cl_2 + H_2O \longrightarrow 2HCl + H_2SO_4$
- $I_2 + Cl_2 + H_2O \longrightarrow HIO_3 + HCl$
- $PbO + H_2O + Cl_2 \longrightarrow PbO_2 + 2HCl$

*
- $C_{10}H_{16}$ (Turpentine oil) $+ 8Cl_2 \longrightarrow 10C + 16HCl$ (Turpentine oil burns in Cl_2. So charring takes place)
- $CH_4 + Cl_2 \xrightarrow{h\nu} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4 + HCl$
- $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

8. With CS_2

$CS_2 + 3Cl_2 \longrightarrow CCl_4 + S_2Cl_2$

9. With HgO:

- $2HgO + 2Cl_2 \longrightarrow HgCl_2 \cdot HgO + \boxed{Cl_2O}$
- $2HgO + 2Cl_2 + H_2O \longrightarrow HgCl_2 \cdot HgO + 2\boxed{HOCl}$

10. Bleaching agent:

- Bleaches by oxidation
- Moist bleaching agent

$$Cl_2 + H_2O \longrightarrow 2HCl + (O)$$

- Permanent bleaching agent.

Tests for Cl_2

- Turns starch iodide paper - blue
- Turns moist litmus red.

Uses:

- Disinfectant, germicide, sterilization of water, bleaching agent
- Used in layer's test

$$Cl_2 + KBr \xrightarrow[CCl_4 / CS_2]{\text{dil. } H_2SO_4} 2KCl + Br_2$$

↓ Brown colour to organic layer

$$Cl_2 + KI \xrightarrow[CCl_4, CS_2]{\text{dil. } H_2SO_4} 2KCl + I_2$$

↓ violet colour to organic layer

- Extraction of Au, Pt etc. (by leaching)
- Industrial solvents : CH_2Cl_2

$CHCl_3$

CCl_4

Westron $Cl_2CH-CHCl_2$

Westrosol $Cl_2C=CHCl$

- Poisonous war gases : $COCl_2$ (phosgene) (enters body and decomposes to CO & Cl_2)

  CCl_3NO_2 (chloropicrin) – Tear gas

  $Cl\,CH_2CH_2-S-CH_2-CH_2-Cl$ – Mustard gas

BROMINE (Br_2)

- Dark red liquid
- BP = 55.8°C
- FP = −7.2°C
- Br_2 vapours are toxic to eyes, throat & nose.
- Br_2 produces painful blisters on skin on skin which take long time to heal.
- When passed through cold water form $Br_2 \cdot 8H_2O$
- Fairly soluble in water.
- Imparts reddish brown colour to organic solvents CCl_4 / CS_2 / $CHCl_3$ / C_6H_6

Prep:

1. $2KBr + F_2 \longrightarrow 2KF + Br_2$

   $2KBr + Cl_2 \longrightarrow 2KCl + Br_2$

   $MgBr_2 + Cl_2 \longrightarrow MgCl_2 + Br_2$

*

2. $5KBr + KBrO_3 + 6H_2SO_4 \longrightarrow 3Br_2 + 6KHSO_4 + 3H_2O$
(or HCl)

3. $2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$

4. $NaBr + H_2SO_4 \longrightarrow NaHSO_4 + HBr$

$HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + H_2O$

} Not suitable for preparing Br_2 as SO_2 is also liberated

5. $NaBr + MnO_2 + H_2SO_4 \longrightarrow Br_2 + NaHSO_4 + MnSO_4 + H_2O$

Chemical properties:

1. With water:

$Br_2 + H_2O \longrightarrow HBr + HOBr$

Bromine water

Bromine water is also a bleaching agent

2. With ammonia:

a) $NH_3 + 3Br_2 \longrightarrow NBr_3 + 3HBr$
(excess)

b) $8NH_3 + 3Br_2 \longrightarrow N_2 + 6NH_4Br$
(excess)

3. With alkalis:

a) $NaOH$ (cold-dil) $+ Br_2 \longrightarrow NaBr + NaBrO + H_2O$

* b) • $6\,NaOH$ (hot conc) $+ 3\,Br_2 \longrightarrow 5NaBr + NaBrO_3 + 3H_2O$ (even with Na_2CO_3, same rxn)

• $Br_2 + Na_2CO_3 \longrightarrow NaBr + NaBrO_3 + H_2O$

* c) $Ca(OH)_2$ (dry) $+ Br_2$ (vap) $\longrightarrow CaOBr_2 \cdot H_2O$

4. With metals

• $2Na + Br_2 \longrightarrow 2NaBr$ (slow)

• $2K + Br_2 \longrightarrow 2KBr$ (fast)

• $2Al + 3Br_2 \longrightarrow 2AlBr_3$ (violent due to high LE)

**** • $Fe + Br_2 \longrightarrow (FeBr_2 + 2FeBr_3) \equiv Fe_3Br_8$

(Ferroso ferric bromide)

5. With non-metals

$2P + 3Br_2 \longrightarrow 2PBr_3$

6. Displacement (oxidation)

$Br_2 + 2KI \longrightarrow 2KBr + I_2$

7. Oxidising properties

• $Br_2 + H_2S \longrightarrow S + 2HBr$

• $Br_2 + SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr$

- $Br_2 + NaNO_2 + H_2O \longrightarrow NaNO_3 + 2HBr$

$Br_2 + Na_3AsO_3 + H_2O \longrightarrow Na_3AsO_4 + 2HBr$

$Br_2 + Na_2SO_3 + H_2O \longrightarrow Na_2SO_4 + 2HBr$

- $Br_2 + Na_2S_2O_3 + H_2O \longrightarrow Na_2SO_4 + S + 2HBr$ (or) $NaHSO_4 + HBr$

- $Br_2 + H_2O_2 \longrightarrow 2HBr + O_2$

8. With MgO

$2MgO + 2Br_2 \longrightarrow MgBr_2 \cdot MgO + \boxed{Br_2O}$

Uses: $2MgO + 2Br_2 + H_2O \longrightarrow MgBr_2 \cdot MgO + 2\boxed{HOBr}$

- Br_2 water - testing unsaturation
- NaBr, KBr are sedatives

IODINE (I_2)

- Violet, lustrous solid.
- Undergoes sublimation
- MP = 114°C
- BP = 184°C (under suitable pressure)
- Produces stains on skin.
- I_2 vapours are pungent and irritating.
- I_2 is insoluble in water but its solubility in water can be increased in the presence of KI.

Slightly soluble in H_2O. Imparts light brown colour.

$KI + I_2 \longrightarrow \underset{\text{Soluble complex}}{KI_3} \longrightarrow K^+ + I_3^-$

- I_3^- is known.

  F_3^-, Cl_3^-, Br_3^- are not known.

- I_2 imparts violet colour to CCl_4, $CHCl_3$, CS_2
- *. I_2 imparts brown colour to alcohol & ether.

} charge transfer from solvent to iodine

Eg: $[C_2H_5\underset{H}{O} \rightarrow I_2]$, $[Me_3N \rightarrow I_2]$

- ***. I_2 imparts blue colour to amylase of starch

  Reason: Linear ~~I_2~~ I_5^- units are held in helical chains of amylase

Prep:

1. $2KI + X_2 \longrightarrow 2KX + I_2$ (X = F, Cl, Br)

*. Oxidants such as F_2, Cl_2, Br_2, H_2O_2, O_3, $KMnO_4$, $K_2Cr_2O_7$, $CuSO_4$ etc can oxidise KI to I_2.

a) $2KI + X_2 \longrightarrow 2KX + I_2$ (X = F, Cl, Br)

b) $2KI + H_2O_2 \longrightarrow 2KOH + I_2$

$2KI + H_2O_2 + H_2SO_4 \longrightarrow K_2SO_4 + I_2 + 2H_2O$

c) $2KI + O_3 + H_2O \longrightarrow 2KOH + I_2 + O_2$

*d) $2I_2 + 9O_3 \longrightarrow I_4O_9 + 9O_2$

(I_2: dry; I_4O_9: ionic, $I^{+3}, 3IO_3^-$, yellow powder)

e) $KI + 3O_3 \longrightarrow KIO_3 + 3O_2$

$KI + 4O_3 \longrightarrow KIO_4 + 4O_2$

f) $I_2 + H_2O + O_3 \longrightarrow HIO_3 + O_2$

g) $2\,CuSO_4 + 4KI \longrightarrow Cu_2I_2 + I_2 + K_2SO_4$

2 mol $CuSO_4 \equiv$ 1 mole $Cu_2I_2 \equiv$ 1 mol I_2

$I_2 + 2Na_2S_2O_3 \longrightarrow 2NaI + Na_2S_4O_6$ (1 e⁻ : I_2 → $2NaI$; 2 e⁻ : $2Na_2S_2O_3$ → $Na_2S_4O_6$)

gm. eq. of I_2 = gm. eq. of $Na_2S_2O_3$

moles of $I_2 \times n_f = \frac{N\,V_{mL}}{1000}$

2. $5KI + KIO_3 + 6H_2SO_4 \longrightarrow I_2 + 6KHSO_4 + 3H_2O$

****
3. $2NaIO_3 + 5NaHSO_3 \longrightarrow I_2 + 3NaHSO_4 + 2Na_2SO_4 + H_2O$

(Caliche) in Chile
salt Petre

4. $KI + H_2SO_4$ (conc) $\longrightarrow KHSO_4 + HI$

$HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$ → not useful since SO_2 is also formed

5. $KI + MnO_2 + H_2SO_4 \longrightarrow I_2 + KHSO_4 + MnSO_4 + H_2O$

Chemical properties:

1. With H_2O:

$$I_2 + H_2O \rightleftharpoons 2H^+ + 2I^- + \frac{1}{2}O_2 \qquad \Delta G^\circ = +ve$$

($\therefore I_2$ is insoluble in H_2O)

- I_2 remains insoluble in H_2O since $\Delta G^\circ = +ve$

$$2H^+ + 2I^- + \frac{1}{2}O_2 \rightleftharpoons I_2 + H_2O \qquad \Delta G^\circ = -ve$$

- The reverse rxn is spontaneous. So, even atmospheric oxygen oxidises I^- to I_2.

2. With ammonia:

$$NH_3 + I_2 \longrightarrow NH_3 \cdot NI_3$$

(Explosive)

$$8\,NH_3 \cdot NI_3 \longrightarrow 5N_2 + 6NH_4I + 9I_2$$

(g) (g) (g)

- Due to liberation of huge no. of gases, it explodes violently.

3. With alkalis:

a) $2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$

(cold dil)

$$NaOI + H_2O \longrightarrow NaOH + \boxed{HOI}$$

b) $6NaOH + 3I_2 \longrightarrow 5NaI + NaIO_3 + 3H_2O$

(hot conc)

4. With metals

$$2Fe + 3I_2 \longrightarrow \underset{\cancel{2FeI_3}}{FeI_2}$$

5. With non-metals:

$$2P + 3I_2 \longrightarrow 2PI_3$$

6. Displacement reactions:

- I_2 cannot displace other halogens from halides but it displaces from halates.

$$2KClO_3 + I_2 \longrightarrow 2KIO_3 + Cl_2$$

$$2KBrO_3 + I_2 \longrightarrow 2KIO_3 + Br_2$$

7. Oxidising properties:

a) $H_2S + I_2 \longrightarrow S + 2HI$

b) $SO_2 + I_2 + 2H_2O \longrightarrow 2HI + H_2SO_4$

c) $2FeSO_4 + H_2SO_4 + I_2 \longrightarrow Fe_2(SO_4)_3 + 2HI$

d) $Na_3AsO_3 + I_2 + H_2O \longrightarrow Na_3AsO_4 + 2HI$

* e) $2Na_2S_2O_3 + I_2 \longrightarrow 2Na_2S_4O_6 + 2NaI$

8. With HgO

- $2HgO + 2I_2 \longrightarrow HgI_2 \cdot HgO + \boxed{I_2O}$
- $2HgO + 2I_2 + H_2O \longrightarrow HgI_2 \cdot HgO + \boxed{HOI}$

9) Reducing properties

$$HNO_3 + I_2 \longrightarrow HIO_3 + NO_2 + H_2O$$

$$Cl_2 + H_2O + I_2 \longrightarrow HIO_3 + HCl$$

$$O_3 + H_2O + I_2 \longrightarrow HIO_3 + O_2$$

Uses:

- Tincture of iodine - $I_2 + KI + C_2H_5OH$
- I_2 - treatement of goitre
- Iodoform test

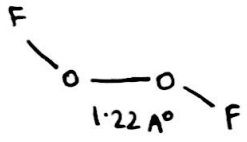
- $I_2 + HNO_3$ (fuming) $+ (CH_3CO)_2O \longrightarrow I(CH_3COO)_2$
- $I_2 + AgClO_4 \longrightarrow IClO_4 + AgI$
- $I_2 + HNO_3$ (conc) $+ H_3PO_4 \longrightarrow IPO_4 \xrightarrow{H_2O} I_2 + HIO_3 + H_3PO_4$

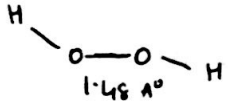
Oxides

1. Oxygen fluorides :

- O_2F_2 (unstable) - orange red liquid

$$O_2 + F_2 \xrightarrow[\text{discharge}]{\text{silent electric}} O_2F_2$$



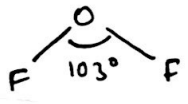


Open-book structure.
non-planar

O-F bond has more p-character

O–O bond length in O_2F_2 < H_2O_2

- OF_2 - yellow coloured gas



Stable at 25° C

- $2NaOH$ (cold dil) $+ 2F_2 \longrightarrow 2NaF + \boxed{OF_2} + H_2O$

- $OF_2 + NaOH \longrightarrow NaF + O_2 + H_2O$

- $OF_2 + H_2O \longrightarrow$ Neutral soln.

OF_2 dissolves in water producing a neutral soln.

- OF_2 is an oxidant.

- OF_2 & O_2F_2 are good fluorinating agents.

$$Pu + 2O_2F_2 \longrightarrow PuF_4 + 2O_2$$

The above rxn helps in separation of Pu from spent nuclear fuel.

2. Oxides of chlorine

Cl_2O, ClO_2, Cl_2O_6, Cl_2O_7, $Cl \cdot ClO_4$

- Oxidants & explosive

3. Oxides of bromine

Br_2O, BrO_2, BrO_3

- Least stable
- Exist only at low temp

** Reason: Middle row anamoly i.e. the filling of d orbitals starts in 4th period. Br possesses completely filled 2d subshell. Due to the poor screening effect, the increase in size from Cl to Br is very less.

4. Oxides of iodine

I_2O_3, I_2O_4, I_2O_5, I_2O_7, I_4O_9

- Solid insoluble oxides
- Decompose on heating

$$I_2O_3 \longrightarrow I^+ + IO_3^-$$

$$I_2O_4 \longrightarrow I^+ + IO_4^-$$

$$I_4O_9 \longrightarrow I^+ + 3IO_3^-$$

- I_2O_5 absorbs CO and is used for estimation of oxygen in organic compounds.

***
Note: • Higher oxides are more stable

- Stability of oxides : I > Cl > Br

Bromine oxides are least stable due to middle row anamoly.

Oxides of Chlorine

Chloro perchlorate ($Cl \cdot ClO_4$)

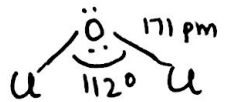
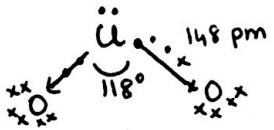
- $CsClO_4 + ClSO_3F \xrightarrow{-44°C} Cl \cdot ClO_4 + CsSO_3F$

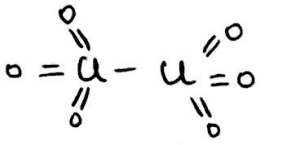
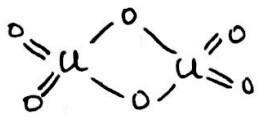
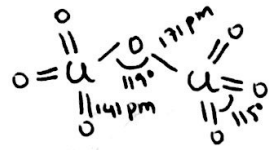
(chloro perchlorate)

- less stable than ClO_2
- $Cl \cdot ClO_4$

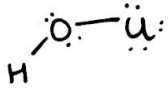
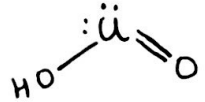
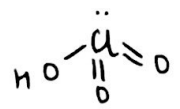
↓ decomposes at room temp.

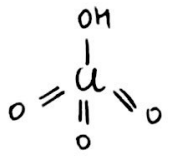
$Cl_2 + O_2 + Cl_2O_6$

Oxide	Prep	Structure	Chem prop	Imp. aspects
Chlorine monoxide (Cl_2O) • Brownish yellow gas • Condenses to orange red liq. upon cooling	• $2HgO + 2Cl_2 \longrightarrow HgCl_2 \cdot HgO + Cl_2O$	 $O \rightarrow sp^3$	• $Cl_2O + H_2O \longrightarrow 2HOCl$ • $Cl_2O \xrightarrow[\text{discharge}]{\text{electric}} Cl_2 + \frac{1}{2}O_2$ • $Cl_2O + 2NaOH \longrightarrow 2NaOCl + H_2O$ • $Cl_2O + NH_3 \longrightarrow N_2 + NH_4Cl + H_2O$ • $Cl_2O + HCl \longrightarrow Cl_2 + O_2 + H_2O$	• Oxidant • Bleaching agent • Explosive • Highly soluble in water
Chlorine dioxide (ClO_2) • Yellow gas • Condenses to dark red liq. upon cooling	• $AgClO_3 + Cl_2 \longrightarrow AgCl + O_2 + ClO_2$ (pure) • $NaClO_2 + SO_2 + H_2O \longrightarrow NaHSO_3 + ClO_2$ (pure) • $NaClO_2 + Cl_2 \longrightarrow NaCl + ClO_2$ • $NaClO_3 + \begin{matrix}COOH\\COOH\end{matrix} \xrightarrow[90°C]{H_2O} ClO_2 + CO_2 + H_2O + Na_2C_2O_4$ • $HClO_3 + HCl \longrightarrow ClO_2 + Cl_2 + H_2O$	 $Cl \rightarrow sp^3d$ • ClO_2 is an odd e^- molecule. ∴ Paramagnetic • It is the only odd e^- molecule which does not dimerize	• $2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$ • $2ClO_2 + NaOH \longrightarrow NaClO_2 + NaClO_3 + H_2O$ • $ClO_2 + NaOH + H_2O_2 \longrightarrow NaClO_2 + O_2 + H_2O$ • $ClO_2 + Na_2O_2 \longrightarrow NaClO_2 + O_2$ • $KClO_3 + HCl \longrightarrow ClO_2 + Cl_2 + KCl + H_2O$	• Oxidant • Bleaching agent • Explosive • Bleaches wood pulp, cellulose, paper & fabrics • Used for water treatment • Euchlorine → ($ClO_2 + Cl_2$) used as bleaching agent • ClO_2 spontaneously catches fire with organic materials paper, cotton etc. • Euchlorine is obtained by treating $KClO_3$ with HCl

Oxide	Prep.	Structure	Chem properties	Imp. aspects
Dichlorine hexa oxide (Cl_2O_6) • Dark red liq. • Condenses into yellow solid at $-180^\circ C$	• $2ClO_2 + 2O_3 \rightarrow Cl_2O_6 + 2O_2$	 (01) 	• $Cl_2O_6 + H_2O \rightarrow HClO_3 + HClO_4$ • $Cl_2O_6 + 2NaOH \rightarrow NaClO_3 + NaClO_4 + H_2O$ * • $Cl_2O_6 + HF \longrightarrow FClO_2 + HClO_4$ • $Cl_2O_6 + N_2O_4 \rightarrow ClO_2 + [NO_2]^+[ClO_4^-]$	• Oxidant, Explosive • In vapour phase exists as ClO_3 (~~dia~~ para magnetic) • In liq. state, exists as Cl_2O_6. • In solid state, exists as $[ClO_2^+][ClO_4^-]$
Dichlorine hepta oxide (Cl_2O_7) • Colourless oily liquid	• $2HClO_4 \xrightarrow[-10^\circ C]{P_4O_{10}} Cl_2O_7$ $(-H_2O)$		• $Cl_2O_7 + H_2O \rightarrow 2HClO_4$ • $Cl_2O_7 + 2NaOH \rightarrow 2NaClO_4 + H_2O$	• Oxidant, explosive • Metastable * • Exothermic oxide of chlorine • Doesn't ignite organic materials. • Most acidic oxide of Cl

Oxo-acids of Cl

Oxo-acid	Prep	Structure	Imp. aspects
Hypo chlorous acid ($HClO$)	• $2HgO + 2Cl_2 + H_2O \rightarrow HgCl_2.HgO + 2HOCl$		• Oxidant • Bleaching agent • Salt : Hypochlorite (OCl^-) • $XO^- \xrightarrow[\Delta]{OH^-} X^- + XO_3^-$ (DPP) • $NaClO$ → household bleaching
Chlorous acid ($HClO_2$)	• $Ba(ClO_2)_2 + H_2SO_4 \xrightarrow[(dil)]{} 2HClO_2 + BaSO_4\downarrow$	 $Cl \rightarrow sp^3$	• Oxidant • Powerful bleaching agent • Salt : Chlorite (ClO_2^-) • $2HClO_2 \xrightarrow{\Delta} HClO + HClO_3$ (DPP) $5HClO_2 \xrightarrow{\Delta} 4ClO_2 + HCl + 2H_2O$ • $NaClO_2$ → commercial bleaching agent
Chloric acid ($HClO_3$)	• $Ba(ClO_3)_2 + H_2SO_4 \xrightarrow[(dil)]{} 2HClO_3 + BaSO_4\downarrow$	 $Cl \rightarrow sp^3$	• Oxidant • Salt : Chlorate (ClO_3^-) • Solubility : $ClO_3^- > BrO_3^- > IO_3^-$ * • Iodates of $Zr^{4+}, Hf^{4+}, Ce^{+4}, Th^{+4}$ are ppt from 6M HNO_3 • $NaClO_3 + H_2O \xrightarrow{\text{Electrolysis}} NaClO_4 + H_2$

Oxo acid	Prep.	Structure	Imp. aspects.
			• $4HClO_3 \xrightarrow{\Delta} 4ClO_2 + O_2 + 2H_2O$ • $5X^- + XO_3^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$ (X = Br, I) (Comproportionation) • $2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$ • $4KClO_3 \xrightarrow[\text{catalyst}]{\text{Absence of}} KCl + 3KClO_4$ • $Zn(ClO_3)_2 \xrightarrow{\Delta} ZnO + Cl_2 + O_2$ • $NaClO_3$ – weed killer • $KClO_3$ – used in fireworks • $HClO_3$, $HBrO_3$ are known only in soln. • HIO_3 is known in both solid & soln phase • $HClO_3$ spontaneously catches fire with paper, cellulose, cotton, silk etc. organic materials
Perchloric acid ($HClO_4$) • Doesn't contain peroxy bond	• $Ba(ClO_4)_2 + H_2SO_4$ (dil) $\longrightarrow 2HClO_4 + BaSO_4\downarrow$ • $KClO_4 + H_2SO_4$ (conc) $\longrightarrow HClO_4 + KHSO_4$ • $ClO_3^- \xrightarrow{\Delta} Cl^- + ClO_4^-$	 Cl → sp^3	• Oxidant • Salt: perchlorate (ClO_4^-) • NH_4ClO_4 → Blasting compound • $Mg(ClO_4)_2$ → Anhydrone (∵ good dessicating (drying) agent) ↳ Used in dry batteries

- $NH_4ClO_4 + HNO_3 \longrightarrow NH_4NO_3 + HClO_4$
- $KClO_4$ - fireworks

** $KClO_4$ - less soluble

- $HClO_4 \cdot 2H_2O + H_2S_2O_7 \longrightarrow HClO_4 + 2H_2SO_4$
- $HClO_4$ explodes upon contact with organic matter.
- $HClO_4$ doesn't undergo DPP since Cl is in max. OS

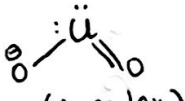
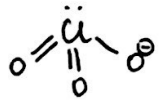
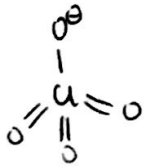
Acid	Anhydride
$HClO$	Cl_2O
$HClO_2 + HClO_3$	ClO_2
$HClO_3 + HClO_4$	Cl_2O_6
$HClO_4$	Cl_2O_7

The following acids are known only in soln:

- $HClO$, $HBrO$, HIO
- $HClO_2$, $HBrO_2$
- $HClO_3$, $HBrO_3$
- $HBrO_4$

- Acidic strength: $HClO < HClO_2 < HClO_3 < HClO_4$
- C.B strength : $ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$
- Oxidising power : $HClO > HClO_2 > HClO_3 > HClO_4$
- Oxidising power : $HOCl < HOBr < HOI$

  Acidic strength, stability : $HOCl > HOBr > HOI$
- Aq $NaClO_4$ → pH = 7
- Aq $NaClO_3$, Aq. $NaClO_2$, Aq. $NaClO$ → pH > 7
- Stability : $HOCl < HClO_2 < HClO_3 < HClO_4$

Oxo anion	Structure	No. of RS	B.O	Bond strength	Stability	Bond length
Hypo chlorite (ClO^-)	$:\ddot{Cl}-O^{\ominus}$ (Linear)	1	1	Inc	Inc	Dec
Chlorite (ClO_2^-)	 (Angular)	2	$\frac{3}{2} = 1.5$			
Chlorate (ClO_3^-)	 (Pyramidal)	3	$\frac{5}{3} = 1.66$			
Perchlorate (ClO_4^-)	 (Tetrahedral)	4	$\frac{7}{4} = 1.75$			

- Oxo-acids of Cl contain $p\pi$-$d\pi$ bonds only.

- Oxidising power of $ClO_4^- < IO_4^- < BrO_4^-$

  $IO_3^- < ClO_3^- < BrO_3^-$ (Middle row anamoly)

  $IO^- < OBr^- < ClO^-$

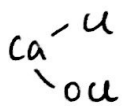
- $FClO_3$ has highest dielectric constant among the gases.

Bleaching powder (Chloride of lime / Calcium hypochlorite)

Manufacture:

Bachmann's plant

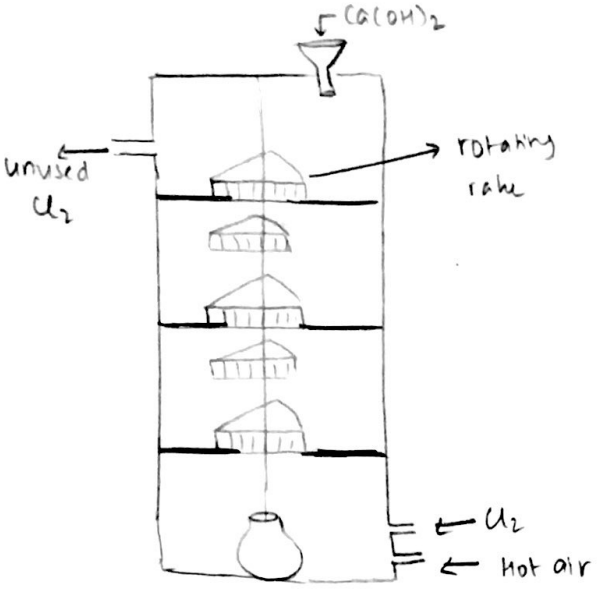
Principle eq: $Ca(OH)_2$ (dry slaked lime) + Cl_2 (dry) $\longrightarrow$ $CaOCl_2 \cdot H_2O$ (Bleaching powder)



$CaOCl_2 \longrightarrow Ca^{+2} + \underset{(-1)}{Cl^-} + \underset{(+1)}{ClO^-}$

- O.S. of Cl in bleaching powder = $-1, +1$ Avg = 0

- Bleaching powder is a mixed salt of chloride & hypochlorite



$Ca(OH)_2 + Cl_2 \longrightarrow CaOCl_2 \cdot H_2O$

- When dry slaked lime is compressed into the chlorinating tower, it moves down slowly and reacts with the upcoming stream of Cl_2 to form bleaching powder which is collected into a pot.
  This rxn principle is called 'principle of counter currents'

*

- Bleaching powder is a delinquescent, yellowish-white powder.
- Composition of bleaching powder = $CaCl_2 \cdot Ca(OCl)_2 \cdot Ca(OH)_2 \cdot H_2O$ ($Ca(OH)_2$: insoluble in water)
- Bleaching powder dissolves in water leaving a residue lime.

Chem properties:

1. With water:

a) $CaOCl_2 \xrightarrow[\text{water}]{\text{cold}} Ca^{+2} + Cl^- + ClO^-$

b) $3CaOCl_2 \xrightarrow[H_2O]{\text{hot}} 3Ca^{+2} + 5Cl^- + ClO_3^-$ (Boiling)

2. With air (auto oxidation)

$$6CaOCl_2 \longrightarrow 5CaCl_2 + Ca(ClO_3)_2$$

3. Catalytic decomposition

$$CaOCl_2 \xrightarrow[\Delta]{CoCl_2} CaCl_2 + \tfrac{1}{2}O_2$$

4. With insufficient dil. acid :

$$2CaOCl_2 + \underset{(dil)}{H_2SO_4} \longrightarrow CaSO_4 + CaCl_2 + \underbrace{2HOCl}_{\downarrow} \\ 2HCl + O_2$$

5. With excess dil. acid

$$CaOCl_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + \boxed{Cl_2}$$

$\boxed{Cl_2}$ ↓ Available chlorine

$$CaOCl_2 + CO_2 \longrightarrow CaCO_3 + \boxed{Cl_2}$$

Available chlorine

- It is the amount of Cl_2 set free when bleaching powder reacts with excess dil. acids or CO_2
- * A good sample of bleaching powder has 35-38% available Cl_2
- The theoretical % of Cl in bleaching powder :

$$\% Cl = \frac{71}{127} \times 100 \simeq 56\%$$

- $$CaOCl_2 + \underset{(excess)}{CH_3COOH} \longrightarrow (CH_3COO)_2Ca + \boxed{Cl_2} + H_2O$$

$$\boxed{Cl_2} + \underset{(excess)}{KI} \longrightarrow KCl + \boxed{I_2}$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

I_2: (+2) → (+2.5) : $1e^-$; $2e^-$ for the two iodine atoms

1m eq. of Cl_2 = gm. eq of I_2 = gm. eq of $Na_2S_2O_3$

gm. eq. of Cl_2 = gm. eq of $Na_2S_2O_3$

$$\frac{W_{Cl_2}}{35.5} = \frac{NV_{mL}}{1000} \qquad (N = M \times 1)$$

$$W_{Cl_2} = \frac{NV_{mL}}{1000} \times 35.5 \text{ g}$$

Wt of $CaOCl_2$ → W_0 gm

Volume of soln. of $CaOCl_2$ → V_0 mL

$$\% \ Cl_2 = \frac{W_{Cl_2}}{W_0} \times 100$$

$$n_{Cl_2} = \frac{W_{Cl_2}}{71}$$

$$n_{CaOCl_2} = n_{Cl_2} = \frac{W_{Cl_2}}{71}$$

$$M_{CaOCl_2} = \frac{n_{Cl_2}}{V_{Lit}} = \frac{W_{Cl_2}}{71} \times \frac{1000}{V_0}$$

Oxidising properties

Bleaching powder is a good OA like Cl_2.

- $CaOCl_2 + PbO \longrightarrow CaCl_2 + PbO_2$
- $CaOCl_2 + NaNO_2 \longrightarrow CaCl_2 + NaNO_3$
- $CaOCl_2 + Na_3AsO_3 \longrightarrow CaCl_2 + Na_3AsO_4$
- $CaOCl_2 + H_2S \longrightarrow CaCl_2 + S + H_2O$
- $CaOCl_2 + FeSO_4 + H_2SO_4 \longrightarrow CaCl_2 + CaSO_4 + Fe_2(SO_4)_3$
- $CaOCl_2 + NH_3 \longrightarrow CaCl_2 + N_2 + H_2O$

- $CaOCl_2 + KI + H_2SO_4 \longrightarrow CaCl_2 + K_2SO_4 + I_2 + H_2O$

Uses:

- Oxidant
- Chlorinating agent
- Bleaching agent similar to Cl_2 (only bleaches in moisture)
- Germicide, disinfectant, sterilization of water
- Prep. of chloroform

$$CH_3CH_2OH / CH_3COCH_3 + CaOCl_2 + H_2O \longrightarrow CHCl_3$$

INTERHALOGEN COMPOUNDS

- These are the binary compounds of two different halogens.
- In interhalogen compounds, the larger halogen (less EN) acts as central atom.
- During hydrolysis of interhalogen compounds, the larger halogen forms oxo acid while smaller halogen (high EN) forms hydrogen halide.

Prep:

- $Cl_2 + F_2 \xrightarrow{200^\circ C} ClF$

  $ClF + F_2 \longrightarrow ClF_3$

  $ClF_3 + Cl_2 \longrightarrow 3ClF$

- $I_2 + Cl_2 \longrightarrow 2ICl$ (liq)

  $I_2 + 3Cl_2 \longrightarrow 2ICl_3$ (or) I_2Cl_6 (liq)

- $Br_2 + 3F_2$ (diluted with N_2) $\longrightarrow 2BrF_3$

  $Br_2 + 5F_2 \longrightarrow BrF_5$ (excess)

  $BrF_3 + Br_2 \longrightarrow 3BrF \xrightarrow{\Delta} BrF_3 + Br_2$

- $I_2 + F_2 \xrightarrow[-45°C]{CCl_3F} 2IF$

  $IF_5 + F_2 \longrightarrow IF_7$

  $I_2 + 7F_2 \xrightarrow[-300°C]{250} 2IF_7$

- $3XeF_2 + I_2 \longrightarrow 3Xe + 2IF_3$

- $KI + 4F_2 \longrightarrow KF + IF_7$

  $PdI_2 + 8F_2 \longrightarrow PdF_2 + 2IF_7$

AX-type

ClF

BrF, BrCl

IF, ICl, IBr

A → ns (⇅) | np (⇅ ⇅ 1) | nd (| | | |) (G.S)

sp3

$:\ddot{\underset{\cdot\cdot}{A}}-X$ (Linear)

Hydrolysis:

$AX + H_2O \longrightarrow HOA + HX$ (+1)

$$ClF + H_2O \longrightarrow HOCl + HF$$

Chemical properties:

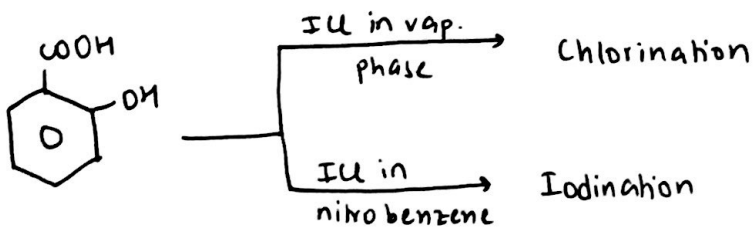
1. ClF is a good fluorinating agent.

- $6ClF + U \longrightarrow UF_6 + 3Cl_2$
- $3ClF + AL \longrightarrow AlF_3 + \frac{3}{2}Cl_2$
- $6ClF + S \longrightarrow SF_6 + 3Cl_2$
- $ClF + SO_2 \longrightarrow ClSO_2F$
- $ClF + CO \longrightarrow COClF$
- $ClF + SF_4 \longrightarrow ClSF_5$

2. ICl → Wij's reagent - used for the estimation of iodine number of oils & fats (iodine no. is a measure of no. of double bonds)

- ICl is a brown solution which when passed through unsaturated oil/fat gets decolourized.

$$\text{>C=C<} + ICl \longrightarrow \text{>C(I)–C(Cl)<}$$

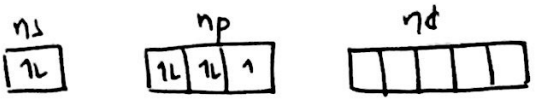
- 

AX_3 type

ClF_3

BrF_3, $BrCl_3$

IF_3, ICl_3, IBr_3

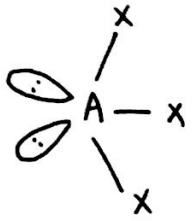
A →  (G.S)

(1st ES)

sp^3d

BL of A–X (axial) > A–X (eq)

$\angle XAX < 90°$

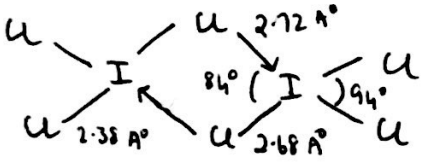


(Bent T-shape) due to repulsions.

***

• ICl_3 exists as I_2Cl_6 - planar dimer

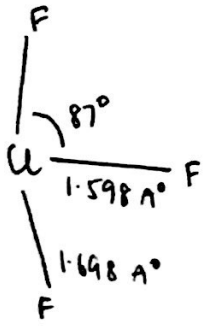
*• $I_2Cl_6 \xrightarrow{77°C} 2ICl + Cl_2$

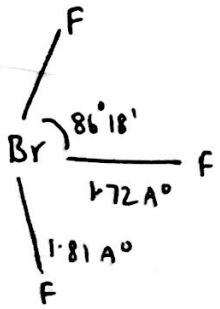


• 3c–4e⁻ molecule

• Planar molecule

•





Hydrolysis

$AX_3 + 2H_2O \longrightarrow HAO_2 + 3HX$

(+3) (+3)

- $BrF_3 + 2H_2O \longrightarrow HBrO_2 + 3HF$

Chem. properties

UF_3

1. F_2 is transported in the form of UF_3
2. UF_3 spontaneously catches fire with wood & building materials like asbestos
3. UF_3 reacts explosively with water, stopcock grease & organic materials like paper, cotton, cellulose etc.
4. UF_3 is a powerful fluorinating agent.
   - $UF_3 + UF_4 \longrightarrow UF_5 + \boxed{UF}$
   - $6UF_3 + 2U \longrightarrow 2UF_6 + 6\boxed{UF}$
   - $4UF_3 + 3Pu \longrightarrow 3PuF_4 + \boxed{2U_2}$
   - $UF_3 + NiO \longrightarrow NiF_2 + \boxed{U_2} + \boxed{O_2}$
   - $UF_3 + MgO \longrightarrow MgF_2 + U_2 + O_2$
   - $UF_3 + Al_2O_3 \longrightarrow AlF_3 + U_2 + O_2$
   - $UF_3 + AgU \longrightarrow AgF_2 + U_2 + \boxed{UF}$
   - $UF_3 + NH_3 \longrightarrow N_2 + U_2 + HF$
   - $UF_3 + N_2H_4 \longrightarrow N_2 + U_2 + HF$

- UF_3 is used as oxidant in short range rocket fuels with N_2H_4.

5.
   - $UF_3 + BF_3 \longrightarrow [UF_2]^+[BF_4]^-$
   - $UF_3 + SbF_5 \longrightarrow [UF_2]^+[SbF_6]^-$
   - $UF_3 + PtF_5 \longrightarrow [UF_2]^+[PtF_6]^-$

BrF_3

1.
- $BrF_3 + UO_2 \longrightarrow UF_4 + Br_2 + O_2$
- $BrF_3 + SiO_2 \longrightarrow SiF_4 + Br_2 + O_2$
- $BrF_3 + TiO_2 \longrightarrow TiF_4 + Br_2 + O_2$

2. BrF_3 is used as a good non-aqueous solvent compared to ClF_3.

Reason: i) Its extent of ionization is more.

$$2BrF_3 \rightleftharpoons [BrF_2]^+ + [BrF_2]^-$$

ii) It is a good fluorinating agent but not violent

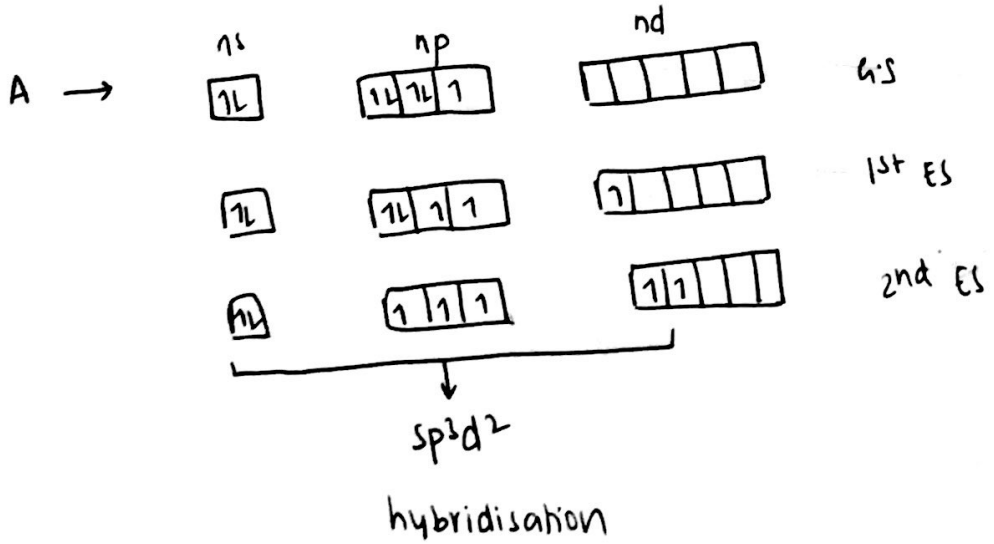
iii) Convenient liq. range: 8·8 – 125° C

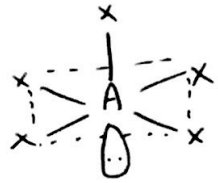
AX_5 type

ClF_5

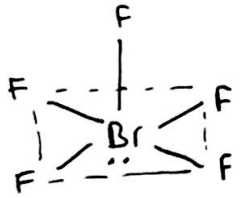
BrF_5

IF_5





Square pyramidal



Hydrolysis:

$$\underset{(+5)}{AX_5} + 3H_2O \longrightarrow \underset{(+5)}{HAO_3} + 5HX$$

** • $ClF_5 + 2H_2O \longrightarrow FClO_2 + 4HF$

• $BrF_5 + 3H_2O \longrightarrow HBrO_3 + 5HF$

Chem. properties

1. $IF_5 \longrightarrow$ less reactive

2. $IF_5 + XeF_2 \longrightarrow IF_5 \cdot 2XeF_2$

$IF_5 + XeF_4 \longrightarrow IF_5 \cdot XeF_4$

Addition compounds.

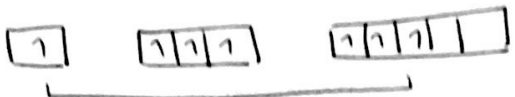
3. ClF_5 & BrF_5 are more reactive that even ClF_3

• $BrF_5 + SiO_2 \longrightarrow SiF_4 + BrF_3 + O_2$

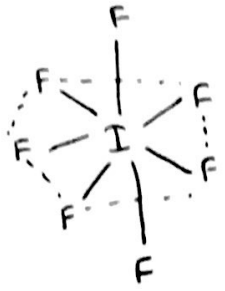
AX_7 type

IF_7

• $KI + F_2$

A →  3rd ES

sp^3d^3



Pentagonal bipyramidal

Hydrolysis:

$$\underset{(+7)}{AX_7} + 4H_2O \longrightarrow \underset{(+7)}{HAO_4} + 7HX$$

* $IF_7 + H_2O \longrightarrow IOF_5 + 2HF$

- $IF_7 + H_2O \longrightarrow HIO_4 \cdot 2H_2O + HF$

(or)

H_5IO_6

Chem property

* $IF_7 + SiO_2 \longrightarrow SiF_4 + 2IOF_5$

Properties of interhalogen compounds

- Covalent
- Interhalogen compounds are more reactive than halogens except F_2.

  Reason: Halogens are non-polar while interhalogen compounds are polar.
- Diamagnetic.
- Coloured (F containing IH compounds are generally colourless)

AX type

ClF (g) – colourless

BrF (g) – pale brown

$BrCl$ (g) – red brown

IF (g) – unstable

ICl (s) – ruby red (α-form)
brownish red (β-form)

IBr (s) – black

AX_3 type

ClF_3 (g) – colourless

BrF_3 (l) – pale yellow / yellow green

I_2Cl_6 (s) – bright yellow / fluffy orange powder

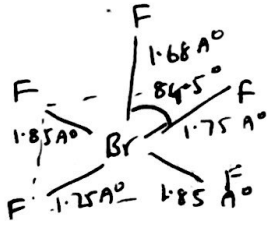
IF_3 (s) – unstable – yellow colour (powder)

AX_5 type

ClF_5 (g) – colourless ((l) per NCERT)

BrF_5 (l) – colourless

IF_5 (l) – colourless (solid below 77K)
(g) per NCERT ×



AX_7 type

IF_7 – colourless
(g)

As mol. wt increases, the colour gets deepened for a particular type of interhalogen compound.

The stability of a particular type of IH compound decreases with increase of EN difference between the halogens, generally

Stability of $IF < BrF < ClF$

Stability of $ClF_3 > BrF_5 > IF_7 > ClF_5 > BrF_3 > IF_5 > BrF > IF_3 > IF$

- These IH compounds behave as non-aqueous solvents due to self-ionizat

- $3\,ICl \longrightarrow [I_2Cl]^+ + [ICl_2]^-$
- $I_2Cl_6 \longrightarrow [ICl_2]^+ + [ICl_4]^-$
- $BrF_3 \longrightarrow [BrF_2]^+ + [BrF_4]^-$
- $2IF_5 \longrightarrow [IF_4]^+ + [IF_6]^-$
- $2ICl \xrightarrow{Py} [I(Py)_2]^+ + [ICl_2]^-$

  $ICN \xrightarrow{Py} [I(Py)_2]^+ + [I(CN)_2]^-$

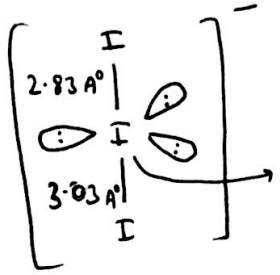
Polyhalogen compounds

These are formed by the action of halogens/interhalogen compounds on the halides.

- $KF + IF_5 \longrightarrow KIF_6$
- $KCl + ICl \rightarrow KICl_2$
- $KCl + ICl_3 \rightarrow KICl_4$
- $KBr + ICl \rightarrow KIBrCl$
- $KI + ICl \longrightarrow KClI_2$
- $KI + 2Cl_2 \longrightarrow KICl_4$
- $KI + I_2 \longrightarrow KI_3$
- $CsF + IF_7 \longrightarrow CsIF_8$
- $CsF + BrF_5 \longrightarrow CsBrF_6$

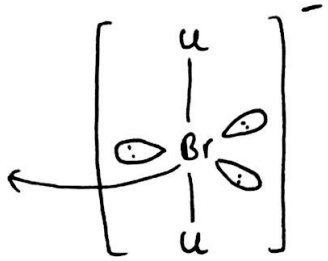
Properties

- Crystalline ionic solids
- Soluble in water.
- Their aq. solns are good electrolytes.
- These are generally coloured



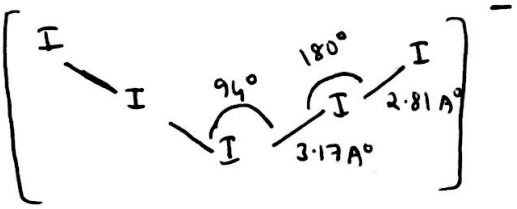
sp^3d

Linear



Tri iodide

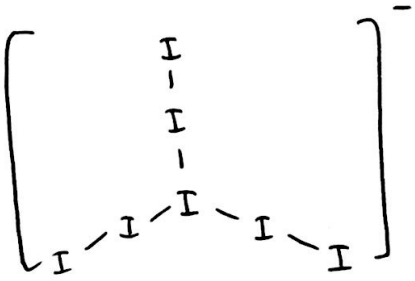
$[BrCl_2^-]$



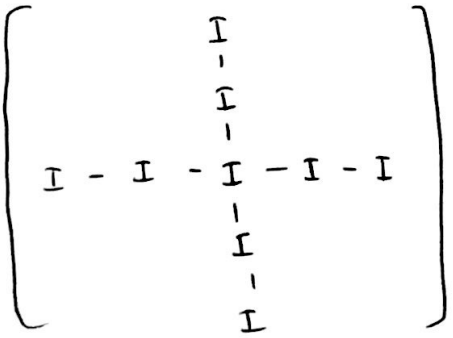
I_5^-

$[I-I-I-I]^{2-}$

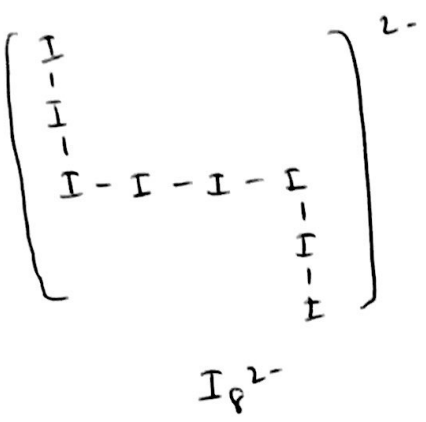
I_4^{2-}



I_7^-



I_9^-



I_8^{2-}

** Stability of $I_3^- > Br_3^- > Cl_3^-$

Decomposition of polyhalogen compounds

- During decomposition of PH compounds, the smaller halogen remains with alkali metal to impart more lattice energy.

- $CsI_3 \xrightarrow{\Delta} CsI + I_2$
- $RbICl_2 \xrightarrow{\Delta} RbCl + ICl$
- $KIBrCl \xrightarrow{\Delta} KCl + IBr$

Displacement reactions

More EN halogen displaces less EN halogen.

- $I_3^- + Br_2 \longrightarrow IBr_2^- + I_2$
- $IBr_2^- + Cl_2 \longrightarrow ICl_2^- + Br_2$

Pseudohalogens

- These are generally the univalent aggregates of two or more EN atoms of which atleast one must be nitrogen.
- These pseudohalogens & pseudohalides exhibit properties similar to halogens & halides respectively.

Pseudohalide ions

CN^-	cyanide	
SCN^-	thiocyanate	
CNO^-	cyanate	
ONC^-	fulminate	
$SeCN^-$	selenocyanate	
$TeCN^-$	tellurocyanate	
$SCSN_3^-$	Azido carbon disulphide	
N_3^-	Azide	
* NCN^{2-}	Cyanamide	(Divalent)

Properties

- $a^- + AgNO_3 \longrightarrow AgCl\downarrow$
  $CN^- + AgNO_3 \longrightarrow AgCN\downarrow$
  → White ppt soluble in NH_3

- $H^+ + a^- \longrightarrow HCl$
  $H^+ + N_3^- \longrightarrow HN_3$
  $H^+ + SCN^- \longrightarrow HSCN$

- $PbCl_4 \longrightarrow PbCl_2 + Cl_2$

  $Pb(SCN)_4 \rightarrow Pb(SCN)_2 + (SCN)_2$

  Thiocyanogen

- $MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$

  $MnO_2 + 4HCN \longrightarrow Mn(CN)_2 + (CN)_2 + 2H_2O$

- $Cl_2 + NaOH \longrightarrow NaCl + NaOCl + H_2O$

  $(CN)_2 + NaOH \longrightarrow NaCN + NaCNO + H_2O$

Preparation of cyanogen

1. $Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$

2. $Hg(CN)_2 \xrightarrow{\Delta} Hg + (CN)_2$

   $AgCN \xrightarrow{\Delta} Ag + (CN)_2$

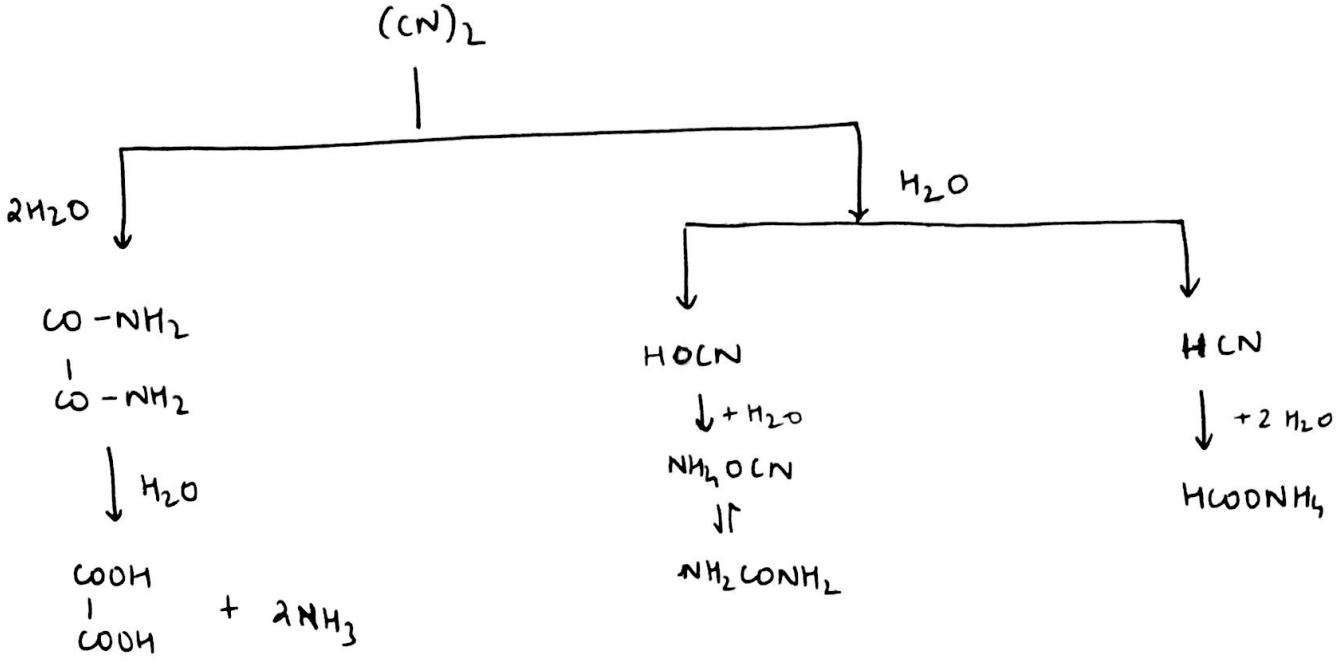
3. • $CuSO_4 + KCN \longrightarrow Cu(CN)_2$

   $2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$

   • $2Cu(SCN)_2 \rightarrow Cu_2(SCN)_2 + (SCN)_2$

4. Electrolysis: Anode: $2CN^- \longrightarrow (CN)_2 + 2e^-$

Hydrolysis of cyanogen



- $[I_2]^+$ → bright blue & paramagnetic
- $[Br_2]^+$ → bright red & paramagnetic
- $I_2 + SbF_5 \xrightarrow{SO_2 \text{ solvent}} [I_2^+][Sb_2F_{11}]^- + SbF_3$
- $Br_2 + BrF_3 + SbF_5 \longrightarrow [Br]^+[Sb_5F_{16}]^-$
- $Cl_2 + ClF_3 + AsF_5 \longrightarrow [Cl_2]^+[AsF_6]^-$

*. Bond length of $[X_2^+] < [X_2]$

- Solubilities: $BeX_2 > MgX_2 > CaX_2 > SrX_2 > BaX_2$ $(X = Cl, Br, I)$

  $BeF_2 > BaF_2 > SrF_2 > CaF_2 > MgF_2$

  $LiF < NaF < KF < RbF < CsF$

- AgF is highly soluble in water